

THE EFFECT OF CO-ACTIVATOR CONCENTRATION ON THE PHOTO-LUMINESCENCE OF ZnS-Cu AT VARIOUS TEMPERATURES

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(Received August 22, 1968)

ZnS-Cu luminophors were produced by sintering together the basic substance, activator and the flux, NaCl, whose concentration ranged from one to eight per cent. The co-activator for this group of luminophors is the chlorine ion. The spectral characteristics of the luminous emission of the samples illuminated by a mercury lamp with a Wood filter were studied with the use of a monochromator and electronic photomultiplier at temperatures of 100, 200, 300, 400, 500 and 600 degrees Kelvin. On the basis of the obtained results it was found that:

1. the co-activator concentration affects the spectral curves of the blue and green bands and their position in the spectrum; with higher concentrations both bands shift toward the shorter wavelengths, which points to a gradual change of the luminophor structure from sphalerite to wurtzite type with increased co-activator concentration;
2. the optimal concentration of introduced flux, at a fixed activator concentration, is between 4 and 5 per cent;
3. the co-activator concentration affects the temperature extinction of the photoluminescence;
4. the co-activator concentration does not bear any observable effect (within experimental error) on the half-widths of the bands at any of the temperatures, nor does it alter the ratio of the widths at higher temperatures to that at 100°K;;
5. the most appropriate model for the photoluminescence of this type of luminophor is that proposed by G. Curie and D. Curie (J. Phys., **21**, 127 (1960)).

1. Introduction

In the ordinary method of producing luminophors by sintering, a flux is introduced besides the basic substance and activator. In ZnS luminophors the most common flux is NaCl, but sometimes LiCl, MgCl₂, BaCl₂ (Zhirov) or a mixture of chlorides (Ostaszewicz 1963) are used. Various quantities of flux are used, for example, B. Levshis (1951) cites two to ten per cent and D. Curie (1960) one to two per cent of NaCl. The flux bears an enormous effect on the luminescent properties of a given material, and a large quantity of flux decreases the brightness of the luminous glow (Levshin (1951)). According to the band theory of semi-

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conductors (Williams 1957), chlorine becomes anchored in the crystal lattice of the luminophor in the place of sulphur and creates donor levels set within the forbidden zone a little below the lower edge of the conduction band. It is known as a co-activator (Lehmann 1957).

It is the purpose of this work to study the effect of the concentration of the chlorine co-activator on the photoluminescence of ZnS-Cu at several temperatures.

2. Experimental procedure

The luminophors were obtained by a method described in an earlier paper (Ostaszewicz 1963). The following ZnS-Cu luminophors were produced:

- I-1 with 1% NaCl relative to ZnS,
- I-2 with 2% NaCl relative to ZnS,
- I-3 with 3% NaCl relative to ZnS,
- I-4 with 4% NaCl relative to ZnS,
- I-5 with 5% NaCl relative to ZnS,
- I-6 with 6% NaCl relative to ZnS,
- I-7 with 7% NaCl relative to ZnS,
- I-8 with 8% NaCl relative to ZnS,

The copper concentration in the mixture used in sintering was constant and equalled 4×10^{-5} gram per gram of ZnS.

The sintering process lasted 20 minutes at a temperature of 970°C. In order to appraise the brightness of the glow of the individual luminophors, their brightness was measured relative to the maximum value by means of a photocell and mirror galvanometer in a manner described earlier (Ostaszewicz 1965). The results of these measurements are given in Table I. We see that the I-4 and I-5 luminophors give the brightest light.

TABLE I
Relative brightness of luminophors

Luminophor	I-1	I-2	I-3	I-4	I-5	I-6	I-8
Brightness in %	66.6	66.6	76.6	100	100	72.6	62.6

The spectral characteristic of the luminous emission relative to a standard (source *A*) was determined by means of an arrangement comprising a Zeiss SPM-1 monochromator, a Zeiss M-12-S photomultiplier and a GES-2-A2 mirror galvanometer. The luminophor was illuminated with an H. P. W.-125W mercury lamp/manuf. Philips, No. 57236 E (70) with a Wood filter transmitting the 365 m μ wavelength. The width of the monochromator's entrance and exit slits was 0.1 mm. The luminophor was illuminated sideways from a distance

of 27 cm, and the distance between the monochromator's entrance slit and the luminophor was likewise 27 cm. The arrangement is shown in the block diagram in Fig. 1.

The intensity distribution as a function of wavelength (the spectral characteristic of the emission) was found for temperatures of 100, 200, 300, 400, 500 and 600 degrees Kelvin. This work was done with the apparatus described in the paper by Kulaszewicz (1969). All spectral characteristics were measured under identical geometrical and electronic condi-

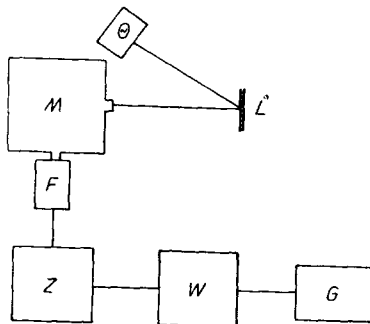


Fig. 1. Block diagram of experimental arrangement, Q — Wood lamp, L — luminophor, M — monochromator, F — photomultiplier, Z — power supply, W — d. c. amplifier, G — mirror galvanometer

tions. The results for the I-1, I-3, I-4, I-5, I-6 and I-8 luminophors are presented in Figs 2, 3, 4, 5, 6 and 7 (all graphs are in the same scale). The results for the spectral characteristics of the I-2 (2% NaCl) and I-7 (7% NaCl) luminophors are not given, as the curves for I-2 are almost identical with those for I-1, whereas the curves of I-7 are intermediate between those for the I-6 and I-8 luminophors.

3. Results and discussion

We see from the figures that the co-activator concentration of the ZnS-Cu luminophors bears a distinct effect on the spectral characteristics of the photoluminescence at the different temperatures.

A. Blue band

At low temperatures (100°K) there appears a blue band, the intensity of which increases and shifts toward the shorter wavelengths as the co-activator concentration increases, up to 5% NaCl (the I-5 luminophor); at the higher co-activator concentrations (the I-6, I-7 and I-8 luminophors) there is a drop in intensity. The maximum of this band corresponds to the wavelength of 450 m μ for the I-1 and I-2 luminophors, and from 442 to 446 m μ for the remaining ones (curve 1 in Figs 2 to 7). With a rise in temperature to 200°K the blue band maximum shifts toward the longer wavelengths and a further rise in temperature extinguishes the entire band (curves 2, 3, 4, 5 and 6 in Figs 2 to 7). The appearance of the blue band at low temperatures and its instability at higher temperatures corroborate their assignment to the presence of the blue copper centers in the luminophors (Levshin 1951)

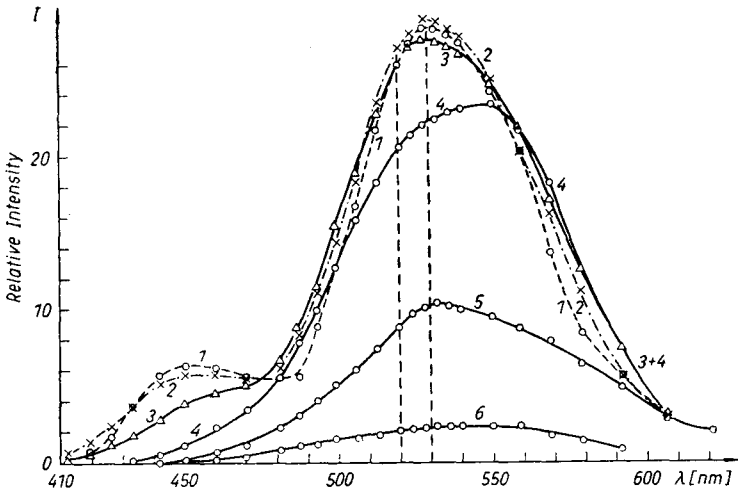


Fig. 2. I-1 luminophor. Spectral characteristic of luminous emission at various temperature, 1 — 100°K, 2 — 200°K, 3 — 300°K, 4 — 400°K, 5 — 500°K, 6 — 600°K

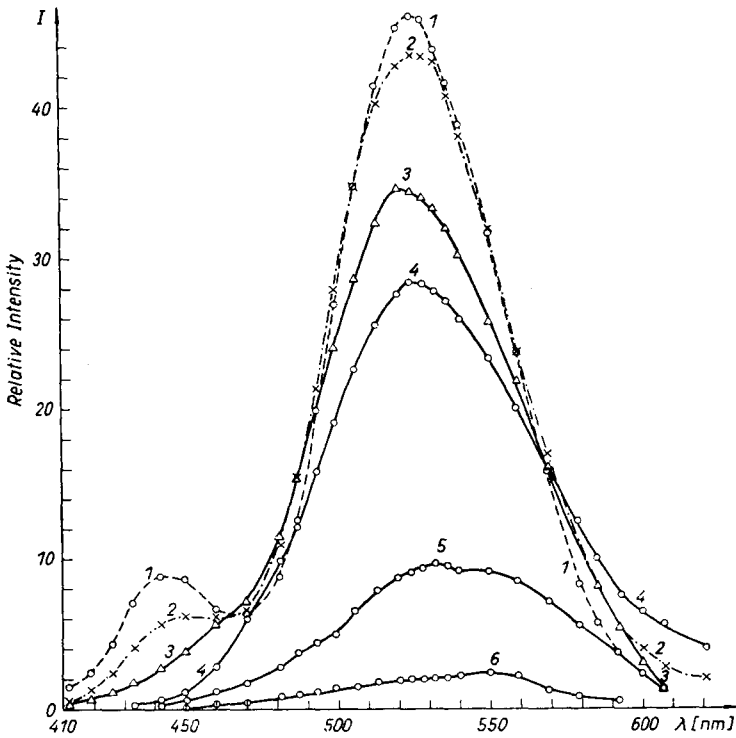


Fig. 3. Curves as in Fig. 2 for I-3 luminophor

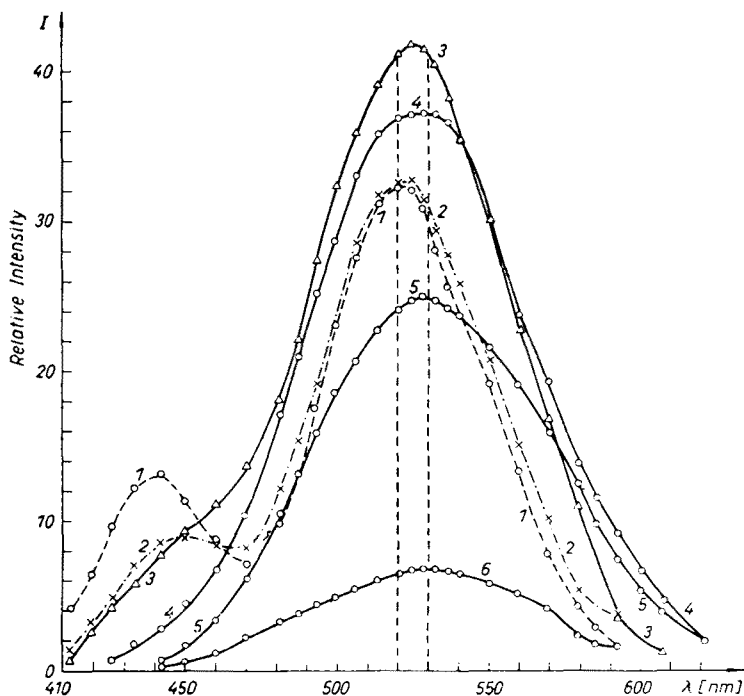


Fig. 4. Curves as in Fig. 2 for I-4 luminophor

and Curie (1964). This is associated with the presence of a wurtzite structure (besides the sphalerite structure) in the crystal lattice of the luminophors. We see thus that the co-activator concentration in these luminophors bears an effect on the position and intensity of the blue band.

B. Green band

In the green band the spectral characteristic of the photoluminescence as a function of co-activator concentration is more diversified. The following features should be noted.

1. At low co-activator concentration (the I-1 and I-2 luminophors) the height of the maxima of the spectral characteristics at temperatures of 100, 200 and 300°K hardly differ from one another (curves 1, 2 and 3 in Fig. 2). In the other luminophors, on the other hand, this regularity fades away (curve 1, 2 and 3 in Figs 4 to 7).

2. In luminophors with low and high co-activator concentrations the highest maxima of the bands appear at the lower temperatures (curves 1 and 2 in Figs 2, 3 and 7). For the intermediate concentrations (the I-4 and I-5 luminophors) the highest maxima appear at room temperature (curve 3 in Figs 4 and 5).

3. Almost all maxima of the green band for the luminophors of higher co-activator concentration, beginning with the I-3 luminophor, lie in the 520 to 530 m μ region. In the I-2 luminophors of low concentration almost all maxima are shifted toward the longer wavelengths. Moreover, in these two luminophors all spectral characteristics are shifted

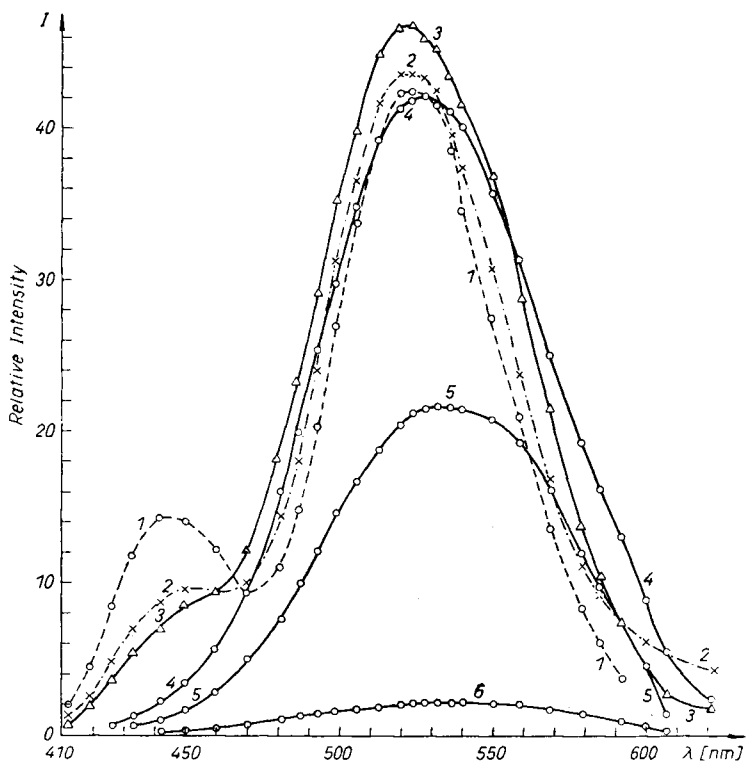


Fig. 5. Curves as in Fig. 2 for I-5 luminophor

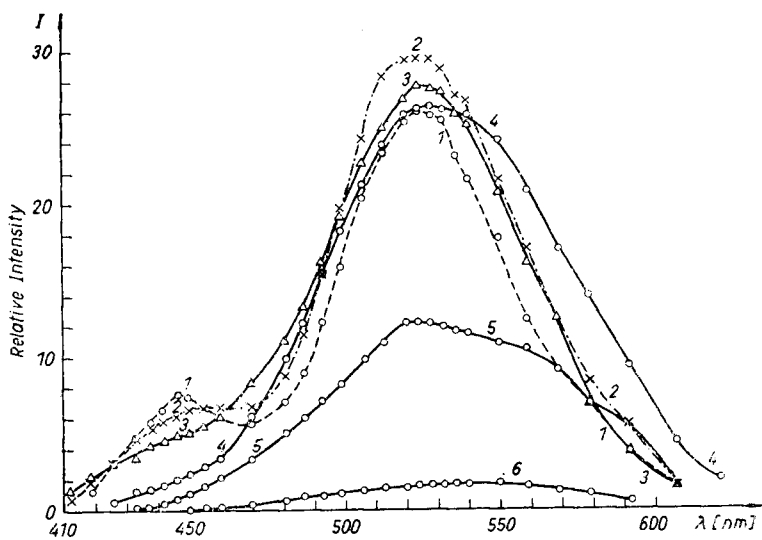


Fig. 6. Curves as in Fig. 2 for I-6 luminophor

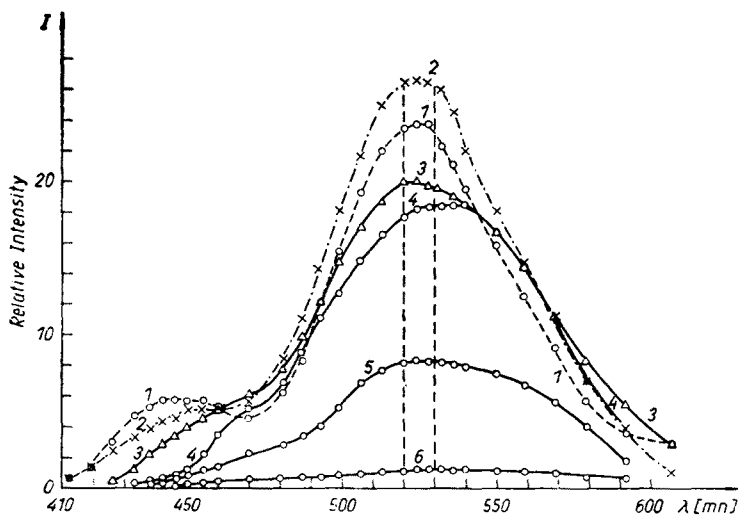


Fig. 7. Curves as is Fig. 2 for I-8 luminophor

toward the longer wavelengths, as compared with the corresponding curves for the remaining luminophors. In order to demonstrate this shift better, the strips between 520 and 530 $m\mu$ are singled out by the dashed lines in Figs. 2, 4 and 7. From these figures we see just how diverse are the ratios of the division of the green band area by these strips in the luminophors of low, intermediate and high co-activator concentrations. It follows that together with increase of concentration the colour of the photoluminescence shifts toward the shorter wavelengths. The shift of the maximum of the green band toward the shorter wavelengths with increasing co-activator concentration proves there is a transformation of the sphalerite structure into a wurtzite structure at higher co-activator concentrations (Curie 1960). The situation is similar when the activator concentration increases, as had been shown in an earlier work (Ostaszewicz 1965).

4. The magnitude of the green band's relative intensity depends on the co-activator concentration in the luminophor. For the I-1 and I-2 luminophors (1 and 2% NaCl) it is small. With increasing co-activator concentration, in the I-3, I-4 and I-5 (3, 4 and 5% NaCl) luminophors, it becomes larger, but a further increase of the concentration, beginning with 6% NaCl (the I-6 luminophor), causes it to drop (Figs 2 to 7). Thus, the optimal weight concentration of the co-activator (at a fixed and given activator concentration) is obtained by introducing 4 or 5 per cent of NaCl into the mixture before sintering the luminophors. Concentrating the co-activator more than this causes a gradual "concentrational extinction" of the photoluminescence.

5. The spectral curves of the luminous glow in the green band primarily have the shape of Gaussian curves, the form of which is more regular for luminophors of intermediate co-activator concentrations (Figs 3, 4 and 5).

6. With a rise in temperature the green band becomes broadened and shifted toward the longer wavelenths for all of the examined luminophors. (Figs 2 to 7). In order to get

a better picture of the effect of temperature on the individual bands, the half-widths (L_e) of all the bands were measured. The results of these measurements are given in Table II. We see here that at any of the temperatures the co-activator concentration does not appreciably affect the half-widths of the bands. At 300°K the widths of the bands range from 770 to 790 Å. (A larger deviation is seen for the I-8 luminophor, for which the width is 850 Å). D. Curie (1964) gives the value of $L_e = 720$ Å as typical for this type of luminophor

TABLE II
Band half-widths *versus* temperature

Luminophor	100	200	300	400	500	600	Temp., in = °K
I-1	665	720	790	840	880	980	Band halfwidths at various tempe- ratures, in Å.
I-2	700	740	790	930	1010	910	
I-3	640	680	770	830	870	750	
I-4	630	690	780	860	930	900	
I-5	650	710	790	910	920	1090	
I-6	635	720	780	920	960	950	
I-8	720	770	850	860	840	1220	

(ZnS, Cu, Cl) at 293°K. Table III gives the band widths at higher temperatures relative to the width at 100°K for all of the examined luminophors. For 300°K this is within the limits of 1.13 to 1.23. Curie cites $L_e(293^\circ\text{K})/L_e(90^\circ\text{K}) = 1.20$ as being a typical value.

7. As regards the temperature extinction of the green photoluminescence the luminophors can be divided into two groups, *i. e.* with weaker (I-1, I-2, I-3 and I-8) and stronger (I-4, I-5 and I-6) photoluminescence. In the former group temperature extinction begins

TABLE III
Ratios of band widths at higher temperatures to width at 100°K

Luminophor	$\frac{L_e(200^\circ\text{K})}{L_e(100^\circ\text{K})}$	$\frac{L_e(300^\circ\text{K})}{L_e(100^\circ\text{K})}$	$\frac{L_e(400^\circ\text{K})}{L_e(100^\circ\text{K})}$	$\frac{L_e(500^\circ\text{K})}{L_e(100^\circ\text{K})}$	$\frac{L_e(600^\circ\text{K})}{L_e(100^\circ\text{K})}$
I-1	1.08	1.20	1.26	1.32	1.47
I-2	1.06	1.13	1.33	1.43	1.30
I-3	1.06	1.20	1.30	1.36	1.17
I-4	1.09	1.23	1.35	1.47	1.43
I-5	1.09	1.21	1.32	1.41	1.67
I-6	1.13	1.22	1.44	1.51	1.50
I-8	1.07	1.18	1.20	1.17	1.70

at 400°K and at 600°K the glow is quite weak (curves 4, 5 and 6 in Figs 2, 3 and 7). In the other group temperature extinction begins at 500°K (curves 5 and 6 in Figs 4, 5 and 6). The I-4 luminophor (4% NaCl) exhibits the weakest temperature extinction effect (curves 4, 5 and 6 in Fig. 4). These results show that the concentration of the co-activator in the luminophor bears a distinct effect of the temperature extinction of the photoluminescence.

Recapitulating the results of this work treating the effect of co-activator concentration on the photoluminescence of ZnS-Cu at different temperatures, we come to the following conclusion: the best model of photoluminescence for this type of luminophor is that proposed by G. Curie and D. Curie (1960). According to this model the blue and green bands have the same ground level, *viz.* the acceptor level of the copper ion. Green emission appears when there are transitions from the donor level which arises due to the co-activator ion, and blue emission from the direct transitions from the conduction band or the center's excited level, to the ground level of the activator. With the assumed model of photoluminescence the importance of the role of the co-activator concentration in the luminophor becomes understandable.

In conclusion the author wishes to express her gratitude to S. Kulaszewicz for designing and constructing the equipment which was used in the performance of the experiments at the different temperatures.

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